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(54) Title: NOVEL POLYOLEFINS AS BLEND COMPONENT (57) Abstract The invention relates generally to blends of polymers comprising a novel flexible polyolefin component produced using a highly specialized catalyst. Use of the novel flexible polyolefins herein disclosed as a component of a blend provides a cost savings to end uses by effectively diluting costly polymeric materials while preserving, and in some cases enhancing, the beneficial physical properties of more costly and highly-engineered polymer compositions.		

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Novel Polyolefins as Blend Component

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TECHNICAL FIELD

This invention relates generally to blends of polymers comprising a novel flexible polyolefin component produced using a highly specialized catalyst. Use of the novel flexible polyolefins herein disclosed as a component of a blend provides a cost savings to end users by effectively diluting costly polymeric materials while preserving, and in some cases enhancing, the beneficial physical properties of more costly and highly-engineered polymer compositions.

BACKGROUND OF THE INVENTION

Polymeric materials, both organic and inorganic, have been included as a component in blend formulations since their discovery. Polymers are not generally suitable for use in their pure form but must rather be blended with other components to achieve multi-functional, value-added products having enhanced physical properties which result from the synergy of the various blend components. These other components may include, but are not limited to: anti-oxidants, so-called "slip" additives, anti-block agents, colorants, inorganic and organic fillers, other polymers, impact modifiers, biocides, adhesion promoters, ultra-violet light stabilizers, crosslinking agents, grafting agents, conductivity-imparters, etc. Virtually any chemical material which is reasonably chemically compatible with a given polymer and which confers desirable properties to the overall blend in which it is a component are potential candidates for use in polymer blends. By employing various unique combinations of components, compounders have made the existence of highly-engineered polymer blends possessing high performance properties

common in the stream of commerce. For purposes of this invention, the word "blend" includes without limitation, the mechanical polyblends, mechanochemical polyblends, chemical polyblends, solution-cast polyblends and latex polyblends as described in the Kirk-Othmer Concise Encyclopedia of Chemical Technology, Volume 24, 3rd ed. Pp 920-922 (Wiley & Sons, NY, ISBN 0-471-86977-5), the contents of which are herein incorporated by reference.

As the level of performance of a given high-value-added polymer material or a blend containing the same is increased, so too in general is increased the relative cost of the material in its raw form. Higher material costs coupled with wastes normally encountered during production can impact the attractiveness of a superior material to the point that the end user is forced by economic factors to accept a less-performing material for a given end use. The long-term effects of these events result in finished goods having reduced work lives, or premature failure of components of various manufactures.

By the instant invention, highly engineered polymers or blends thereof are mixed with the novel polyolefin material herein disclosed. Such an admixture effectively dilutes the polymer or blend to a level at which the polymer or blend retains the inherent beneficial physical properties of the mother material. Since the novel polyolefins of this invention are relatively inexpensive, cost savings are significant enough to permit use of highly-engineered polymers or blends containing the same in applications where their previous employment was economically prohibited.

Accordingly, it is an object of this invention to provide a diluent material comprising the novel polyolefins herein disclosed for highly engineered polymers and blends which contain the same which is reasonably compatible with a wide range of polymeric materials and their blends.

It is a further object to provide a diluent material which is itself relatively low in cost.

It is a further object of this invention to provide blends containing high value added polymeric compositions which necessarily have a reduced raw material cost on a weight basis

for end users of the blends, owing in part at least to the use of the novel polymeric compositions herein disclosed.

It is a further object still of this invention to permit use of highly engineered polymeric compositions in applications which raw material costs would otherwise be prohibitive of their use, thus increasing the quality of various articles of manufacture.

SUMMARY OF THE INVENTION

The blends of this invention comprise generally at least one commercially-available high-value-added, highly engineered organic polymer product, thermoplastic, or a blend containing the same. The blends are useful as raw materials for use in producing articles of manufacture using conventional plastic-forming processes which include, but are not limited to: injection molding, blow molding, extrusion, thermoforming, and vacuum forming.

An example of a blend containing an engineered thermoplastic is a material known as "Santoprene" (TM) which in this case is a thermoplastic vulcanizate (TPV) consisting essentially of a polypropylene, kaolin, oil, with the balance being an olefinic rubber copolymer, including one of EPDM (Ethylene-Propylene-Diene-Monomer) rubber or EP (Ethylene-Propylene) rubber. This material is available from Advanced Elastomer Systems ("AES"), 388 South Main Street, Akron, Ohio in a variety of commercial grades containing, inter alia, varied amounts of the aforesaid ingredients dependent upon the specific intended use. These materials are more fully described in AES General Product Bulletin TPE-02-12, the contents of which are herein incorporated by reference.

Another example of an engineered polymer blend is the material known generically as Kraton (TM), available from Shell Chemical Company, Two Shell Plaza, Houston, Texas. Kraton (TM) polymers are divided into classes: the Kraton (TM) D series materials which include styrene-butadiene-styrene and styrene-isoprene-styrene, the Kraton (TM) G series materials which include styrene-ethylene/butylene-styrene. Another class includes the radial (A-B)_n type polymers styrene-butadiene,

styrene-isoprene. Still yet another class of these materials includes Styrene-butadiene, styrene-ethylene/propylene, and styrene-ethylene/butylene. Essentially, these polymers all contain a styrenic end-block and a rubber midblock portion, and have varied degrees of crosslinking within their matrices which provide a family of materials having diverse physical properties useful in a wide range of specific applications. Typically these materials have the strength of rubber but do not require vulcanization. They are described in Shell product bulletin SC:68-96, the contents of which are herein incorporated by reference.

Another example of an engineered polymer blend includes the family of materials known as Hytrel (TM), marketed by DuPont Engineering Polymers, 713 Chestnut Run Plaza, Wilmington, Delaware. These materials are composed of polyether-ester block copolymers of polybutylene terephthalate and long-chain polyether glycols having varied segment hardnesses and chain lengths, and are described in DuPont bulletin H-57473, which is herein incorporated by reference.

Still yet another example of an engineered polymer blend is the material known as "Primacor" (TM), available from the Dow Chemical Company, 2040 Willard H. Dow Center, Midland, Michigan. These materials are acrylic acid/ethylene copolymers and are more fully described in Dow brochure 305-01618-489, which is herein incorporated by reference.

Other engineered plastic materials include the elastic, substantially linear olefin polymers described in US patent no. 5,272,236; ultra low density copolymers known as "Attane" (TM) available from Dow Chemical Co., 2040 Dow Center, Midland, Michigan and described in their brochure no. 305-1596-1192X SMG, the entire contents of which are herein incorporated by reference; polyethylene resins, including but not limited to those known as DOWLEX (TM) 3010, DOWLEX (TM) 2500, 2503, 2505, 2507, 2517, 2535, 2553, IP-2580 available from Dow Chemical Co., at the same address already given and described in their product brochures 305-01703-695X RJD, form 305-01704-695X-RJD, 305-1661-396-X RJD, 305-01662-396X RJD, 305-01663-396X RJD, 305-01664-396X RJD, 305-01955-396X RJD, 305-01665-396X RJD, 305-01666-396X RJD, 305-01667-396X RJD, 305-01994-396X RJD,

the contents of which are herein incorporated by reference; linear low density polyethylenes (LLDPE), high density polyethylenes (HDPE); and acrylonitrile-butadiene-styrene polymers.

A process known as "dynamic vulcanization" is regularly practiced by those skilled in the polymer art. This process comprises a blending procedure wherein a plastic material, such as, for example a polyolefin, is intensively mixed together with a rubber material at about 33 parts of plastic material to 66 parts of rubber material in, typically, an internal mixer at a temperature greater than the melting point of the plastic. After the melt-mixing, vulcanizing agents such as sulfur, peroxides, radiation, etc., are added until the mixing torque peaks at which time the mix is dumped, cooled, and granulated. This process produces a two-phase structure in which the rubber is in the form of small (1 to 2 micron) particles which are embedded in a sea of the plastic material. This process can be typically employed to produce elastomeric alloy thermoplastic vulcanizates. The rubber materials can comprise natural rubbers, EP and EPDM rubbers, nitrile rubbers, and virtually any other rubber substance.

Thermoplastic vulcanizate materials may be contrasted to elastomeric alloy melt-processible rubbers which are single-phase combinations of two or more polymer systems, for example, a mixture of chlorinated polyolefin with ethylene-vinylacetate copolymer and an acrylic-ester rubber gives a material sold by E.I. DuPont de Nemours of Delaware as Alcryn (TM). These types of materials generally have lower processing temperatures than thermoplastic vulcanizates and can hence be advantageously processed using conventional rubber-processing equipment.

For purposes of the instant invention and the appended claims the words "engineered polymer" includes: 1) Thermoplastic resins, i.e., any resin or plastic compound that, as a finished material is capable of being repeatedly softened by heating and hardened by cooling and which may contain at least one of the following resin materials (either substituted or unsubstituted, containing a substituting element selected from the group consisting of halogen, methyl, alkyl, alkenyl, carboxyl, alkoxy, amino, amido, imino, or nitrilo): acetal, acrylic, cellulosic,

chlorinated polyether, fluorocarbons, polyamides (nylons), polycarbonates, polyethylene, polypropylene, polystyrene, polyurethanes, and vinyl resins; 2) Thermoplastic elastomers, i.e., any of a family of polymers that resemble elastomers in that they are highly resilient and can be repeatedly stretched to at least twice their initial lengths with full, rapid recovery, but are true thermoplastics and thus do not require curing or vulcanization; 3) Thermoplastic polyesters, i.e., any of a class of linear terephthalate polyesters that are true thermoplastics including polyethylene and polypropylene terephthalate, polybutylene terephthalate, and polycyclohexylenedimethylene terephthalate;

4) Thermoplastic polyolefins, i.e., any of a group of elastomers which may include either substituted (e.g. polyvinyl chloride) or un-substituted components, produced by either: i) melt-blending polypropylene with between about 15 % to 85 % of a material selected from the group consisting of terpolymer elastomer, ethylene-propylene rubber, or styrene-butadiene rubber; or ii) copolymerizing propylene with ethylene-propylene elastomer in a series of reactions; 5) Thermosetting plastics (thermosets), i.e., resin or plastic compounds which may or may not be liquids at some stage in their processing, which are cured by heat, catalysis, or other chemical means, which include much crosslinking and are in their final state substantially infusible and insoluble, including normally thermoplastic materials which have been rendered unmelttable by means of crosslinking treatments or reactions, including: alkyd, allyl, amino, epoxy, furane, phenolic, polyacrylic ester, polyester, and silicone resins; 6) Thermoplastic vulcanizates, i.e., materials which are produced using the well-known dynamic vulcanization process whereby a rubber is vulcanized during its melt mixing with a molten non-crosslinking plastic, with the rubber being selected from conventionally known rubbers and the molten non-crosslinking plastic typically belongs to the family of materials described above as thermoplastic resins; 7) cyclo-olefin copolymers produced by copolymerizing alpha olefins having between 2 and 12 carbon atoms with cyclo olefins including: dicyclopentadiene, cyclo-octene, tetracyclododecene, or norbornene with another alpha olefin monomer, whether they be

microcrystalline and resulting from polymerizations of alternating monomer sequences, or amorphous materials which result from random copolymer distribution; and 8) polyolefinic graft copolymers containing a grafted monomer including at least one of: maleic anhydride, acrylic acid, methacrylic acid, vinyltrimethoxy silane, acrylamide, itaconic acid, fumaric acid or its anhydride, monomethyl maleate, monoethyl maleate, vinyl amines and amides, and other substituted vinyl monomers that are capable of free radical polymerization onto FPO polymers and copolymers, using techniques well known to those skilled in the art including, without limitation, the teachings of US Patents 3,687,849; 3,687,905; 4,160,739; 5,001,197; 5,420,303; 5,538,510; and 5,551,974, the contents of which are herein incorporated by reference. These are all graft copolymers which are useful and may be employed as an additive in a sufficient amount to cause compatibility between the dissimilar blend components, or, alternatively, the graft copolymer of an FPO homo or copolymer with a maleic acid or other aforementioned graft candidate itself may be employed as a predominant component of the blend. Maleic acid or anhydride is widely used as a graft monomer because of its low cost and its role of providing incorporation of functionality onto polymers by which other groups may be added to the polymer backbone by further reaction of the carboxyl groups with, for example, hydroxy compounds or nitrogen compounds.

The graft copolymer of an unsaturated acid with FPO propylene homopolymer or copolymer may also be reacted with various organic nitrogen compounds (amines, imines, amides, etc., whether straight chain, branched, cyclic, and whether or not they also contain other atoms in their molecular structures including without limitation, sulfur, oxygen, halogens, or other elements of sufficient electronegativity (Pauling) to impart effective polarity to the graft copolymer molecules as a whole and thus tend to promote compatibility of blend components not otherwise compatible with one another.

In cases where it is desired to blend the polymers of this invention with other polymeric materials with which the FPO polymers are not compatible, various compatibilizers well-known to those skilled in the art of polymer blending may be employed.

The graft copolymers just described are one example. However, compatibilizers may also comprise styrene copolymerized with acrylic acid or its derivatives, or any well-known material which includes polar and non-polar sub-portions (polarphillic and polarphobic), each having compatibility with one of the components of the desired blend suffice to marry the materials. These compatibilizers are believed to function in an analogous fashion to micellular soaps, the molecules of which contain both a hydrophillic and a hydrophobic portion wherein the bifunctionality tends to promote homogeneity between two otherwise dissimilar materials. It is well known that polypropylene may exist in either a crystalline form or an amorphous form. Crystalline polypropylene generally has an isotactic or syndiotactic structure and that amorphous polypropylene generally has considerable atactic structure. The novel polymeric materials ("FPO" polymers) suitable as a component in the polymer blends of this invention are composed predominantly of polypropylene having a crystallinity between that of amorphous polypropylene and crystalline polypropylene. U.S. Pat. Nos. 3,112,300 and 3,112,301, for example, describe isotactic polypropylene and provide structural formulae for isotactic and syndiotactic polypropylene. Conventional polymers of this type typically have a crystallinity, or heat of fusion, of 75 Joules per gram (J/g) or higher, and more typically 90 J/g or higher. Amorphous polypropylenes, on the other hand, are tacky solid (at room temperatures), low molecular weight polymers having a low to very low level of crystallinity, less than about 3.0 Joules per gram and often less than 1.0 Joules per gram.

In order to produce polyolefins, a monomeric alpha olefin raw material is generally contacted with a suitable catalyst under conditions of pressure and temperature sufficient for causing a polymerization of the monomer. Great volumes of investigation in the field of polymerization catalysis have yielded a multitude of polymeric products having a wide range of physical and chemical properties. By modifications to the catalyst and reaction conditions it is possible in some instances to produce materials especially suitable for a particular application.

Of the various known catalysts used for polymerizing olefins, the prior art patents forthwith presented disclose one type of catalyst used in the formation of such polymers. They include generally a pro-catalyst that is typically formed from the reaction product of a magnesium alkoxide compound of the formula MgR_1R_2 where R_1 is an alkoxy or aryl oxide group and R_2 is an alkoxide or an aryl oxide group or halogen, and a tetravalent titanium halide wherein the reaction takes place in the presence of an electron donor and, preferably, a halogenated hydrocarbon. These include: U.S. Patent Nos. 5,118,768 ; 5,164,352 ; 5,089,573 ; 5,118,649 ; 5,118,767 ; 5,294,581 ; 5,118,768 ; 5,164,352 ; 5,438,110 ; 4,990,479 ; 5,218,052 ; 5,182,245 ; 5,153,158 ; 4,990,477; and in European Patent 475,307.

Detailed Description of the Invention
Including a Preferred Embodiment

The present invention is directed to multi-component blend formulations useful in producing various articles of manufacture. The blends comprise a novel polyalphaolefin polymer which is prepared by polymerizing an α -olefin monomeric raw material in the presence of a catalyst comprising the reaction product produced from the combination of a first catalyst component and a second catalyst component. The first catalyst component comprises an intimate anhydrous mixture of a magnesium halide, an aluminum halide, and a silane made preferably by ball milling the magnesium halide with the aluminum halide and then adding the silane component, and subsequently ball milling the resultant three component mixture further. Subsequently, a titanium halide which is preferably tetravalent, is added along with a nitrogen-containing organic compound and further ball milling is commenced which finally yields what is referred to by some in the art as a "pro-catalyst". The pro-catalyst is subsequently mixed with a second catalyst component which includes an organometallic compound, preferably tri-ethyl aluminum, to produce the final active catalyst material by which the polymers used as a blend

component of this invention are derived by polymerization of an alpha-olefin. Optionally, a second silane material may be added to the finished catalyst to assist in controlling the crystallinity of the novel polymeric blend component herein disclosed. Polymerization is then effected by means known to those skilled in the art.

The flexible polyolefin component of the blends according to this invention may be comprised of a polymer prepared from a wide variety of monomeric raw materials. For example, one or more monomers selected from the group of alpha olefins including: propylene, ethylene, 1-butene, 1-pentene, 1-octene, or mixtures thereof may be employed as feedstocks. These feedstocks are provided in the raw material feed in an amount between about 1 to 20 weight percent based on the total weight of the monomer charge, when propylene is used as the major component of the monomer charge. When it is desired to produce FPO copolymers for use as blend components in accordance with this invention, all which is necessary is to provide the comonomer as part of the feedstock, and such is well within the scope of the capabilities of one of ordinary skill in the polymer art. It is generally true that in order to produce an FPO copolymer containing, for example, ethylene in the finished polymer, one uses an amount of ethylene in the raw material feed which is in slight excess to its desired content in the finished polymer. That is, to produce a copolymer containing 10 % ethylene, one needs to use a monomer feed which contains approximately 10.5 % of ethylene, owing to factors which control what is well-known and referred to in the art of polymerization as "conversion efficiency". It is also desirable to include hydrogen in the raw material feed in an amount not to exceed about 10 weight percent in order to control the chain length of the resultant polymer.

The blends according to this invention may be produced by mixing the various components while they are in the solid state and then adding them to a screw-type extruder in which they are melted and blending is effected by the mechanical motion of the screws, or the components may be sequentially added to a melting-pot arrangement and mixed using mechanical means well-known to those of ordinary skill in chemical blending, either in the presence or absence of solvents.

The Novel Component Composition

A new catalyst capable of producing a new class of polymers, (flexible polyolefins, or "FPO's"), has, by virtue of recent investigative efforts been created and discovered to yield a controllable degree of crystallinity in polyolefin polymers lower than that found in commercial isotactic polypropylene. This class of polymers has been unexpectedly found to yield a blend component for polymer blends products having enhanced physical properties over blend products produced from prior art catalysts and methods.

The catalyst employed for the production of the FPO polymers used as a component of blends in accordance herewith includes a pro-catalyst component which is combined with a co-catalyst component in order to form the finished catalyst material to which an external modifier compound may optionally be added. The pro-catalyst includes a magnesium halide, an aluminum halide, a tetravalent titanium halide, a particular nitrogen-containing organic compound which functions as an electron donor, and an internal modifier that is typically a silane component. The co-catalyst is an organometallic compound. The external modifier is a second silane compound.

Catalyst preparation begins with the magnesium halide and aluminum halide being combined, preferably with some degree of mixing, for example, by ball milling. The mixing is carried out at about room temperature, although the exact temperature is not a crucial aspect of catalyst preparation. The silane component, or internal modifier, is typically a liquid and is added to these halides either before or after they are mixed.

The silane and halides are preferably mixed by pulverization in a ball mill to form a first mixture before additional components are added. Suitable milling of these pro-catalyst components is readily accomplished in a 1L stainless steel rotary mill pot filled to about 50 volume percent with 1/2" stainless steel balls.

After the initial ball milling, the electron donor and a titanium halide are combined with the halide and silane mixture. The specific amounts added are determined relative to the other catalyst ingredients, and fall within the atomic ratio range set forth below. The donor and titanium halide are both preferably liquid, and may be added at once or slowly to the other catalyst

ingredients. These are preferably sprayed into the ball mill or other vessel, although any means of addition is acceptable. The combination of the electron donor, titanium halide, and first mixture comprising silane and mixed halides of magnesium and aluminum is then mixed, preferably by ball milling, in order to form the pro-catalyst. It is preferred that the mixing occur over a period of about 4 to 40 hours, more preferably about 8 to 30 hours, and most preferably about 12 to 25 hours.

After milling the pro-catalyst, a co-catalyst is added to provide an active catalyst material suitable for producing core layer polymers according to the instant invention. An optional external modifier (which is also a silane) may be subsequently added to the active catalyst material to modify the catalyst and enable it to produce flexible polyolefins having reduced tackiness.

The relative amounts of each component in the catalyst can vary over well defined ranges. Specifically, the molar ratio of Mg:Al:Si:N:Ti is about 8:0.01:0.01:0.2:1 to 80:30:0.5:1.2:1, preferably 12:1:0.1:0.3:1 to 70:25:0.4:1:1 Mg:Al:Si:N:Ti. In a more preferred embodiment, the molar ratio of Mg:Al:Si:N:Ti is about 14.9:1.9:0.2:0.6:1. In these ratios, Mg, Al and Ti designate atomic contributions of these elements from halides, Si designates the silicon contribution from the silane component, and N designates the nitrogen contribution from the internal donor.

Any titanium halide is suitable for mixing with the magnesium and aluminum halides, although titanium tetra-halides are preferred and titanium tetrachloride is the most preferred. Although any aluminum halide is suitable for use in the catalyst, aluminum trichloride is preferred. Similarly, although any magnesium halide is suitable for use in the catalyst, magnesium di-chloride is preferred. The titanium halide is preferably a liquid when added, as are the electron donor and the silane component.

The nitrogen-containing organic compounds function as internal electron donors and are classified as being either Type I or Type II. Type I internal donors are used to increase the pro-catalyst surface area and accordingly the catalyst activity. Type II internal donors are used to increase the molecular weight and reduce the low molecular weight ("LMW") fractions that cause the stickiness typically associated with poly-olefin polymers. It has now been found that some weak Lewis bases, such as certain

nitrogen-based donors like 2,6-lutidine and 6-chloro-2-picoline, are effective as Type II donors to increase the molecular weight of polymers without significantly affecting the crystallinity of the polymers produced. Although any internal electron donor is suitable for use in the catalyst, the Type II internal donor is preferably a nitrogen-based Lewis base. The internal donor is more preferably selected from the following: 2,3-dimethylquinoxaline, quinaldine, 2,6-lutidine, 2,4,6-collidine, tetramethylpyrazine, 2,4-dimethylquinoline, 2,6-dichloropyridine, 2-chloroquinoline, 2-chloro-6-methoxypyridine, 2,3-dichloroquinoxaline, 2,4,6-trichloropyrimidine, 2,4,5,6-tetra-chloropyrimidine, 2-chlorolepidine and 6-chloro-2-picoline, and the donor is most preferably 2,6-lutidine, 2,6-dichloropyridine, 6-chloro-2-picoline, or mixtures thereof. The amounts of internal electron donor used is relative to amounts of other ingredients in the catalyst recipe. Therefore, amounts of the various components must be quantified by the molar ratio relative to each other.

The co-catalyst component, which is an organometallic compound, and preferably a metallic alkane free of halogens, may be chosen from organoaluminum compounds. Dialkylaluminum halides and dialkylaluminum alkoxides may be used, but it is preferable to use aluminumtrialkyl compounds, more preferably those wherein each of the alkyl groups has between 1 and 6 carbon atoms, e.g., aluminumtrimethyl, aluminumtriethyl, aluminumtri-n-propyl, aluminumtri-isobutyl, aluminumtri-isopropyl and aluminumdibutyl-n-amy. Alternatively, these may be used in combination with various alkyl aluminum halides, e.g., diethyl aluminum chloride. In the most preferred embodiment, aluminum triethyl is used as the co-catalyst.

The internal modifier silane component has a formula of $R_1R_2Si(OR_3)(OR_4)$, wherein R_1 and R_2 are each an H, C_{1-6} alkyl, aryl, C_{6-12} cycloalkyl, each of which may be unsubstituted, mono- or di-substituted, and R_3 and R_4 are H, C_{1-6} alkyl, or a mono- or di-substituted C_{1-6} alkyl. A preferred aryl is C_{6-22} aryl. Preferably, R_1 is C_{6-12} cycloalkyl or a mono- or di-substituted C_{6-12} cycloalkyl, R_2 is H or methyl, more preferably R_1 is an unsubstituted C_{6-12} cycloalkyl, and most preferably is cyclohexyl. R_2 is more

preferably methyl. R_3 and R_4 are preferably an unsubstituted C_{1-6} alkyl, more preferably methyl or ethyl, and most preferably methyl. The amount of silane specified above is preferably added by spraying over the halide combination, or some other form of vaporizing, to increase the surface area and contact between the components.

The external modifier may be any silane modifier, but is preferably a silane having a formula of $R_1R_2Si(OR_3)(OR_4)$, wherein R_1 and R_2 are each an H, C_{1-6} alkyl, aryl, C_{5-12} cycloalkyl, each of which may be unsubstituted, mono- or di-substituted, and R_3 and R_4 are H, C_{1-6} alkyl, or a mono- or di-substituted C_{1-6} alkyl. A preferred aryl is a C_{6-13} aryl. Preferably, R_1 is C_{6-12} cycloalkyl or a mono- or di-substituted C_{6-12} cycloalkyl, R_2 is H or methyl, more preferably R_2 is an unsubstituted C_{6-12} cycloalkyl, and most preferably is cyclohexyl. R_3 is more preferably methyl. R_3 and R_4 are preferably an unsubstituted C_{1-6} alkyl, more preferably methyl or ethyl, and most preferably methyl.

Most preferably, the external modifier is identical to the internal modifier used in the pro-catalyst. Increasing the amount of external modifier typically increases the crystallinity in the polymer ultimately produced. The pro-catalyst with co-catalyst in the absence of an external modifier is capable of producing an FPO polymer with a H_f at a lower range of about 4.6 J/g to 60 J/g, preferably around 15 J/g to 30 J/g, and this may be adjusted upward by increasing the amount of external modifier added to the catalyst up to an H_f of about 60 J/g, and every whole integer therebetween. The external modifier may be added in any desired ratio to advantageously provide the desired crystallinity in the FPO polymers, although the molar ratio of Si:Ti (external silane modifier to titanium in the pro-catalyst) will typically be from 0:1 up to about 4:1, and more typically be from 0:1 up to about 1:1. The preferred amount of external modifier is seen in the Examples below, although other useful amounts may be readily determined without undue experimentation by those of ordinary skill in the art after reading this specification.

Besides increasing crystallinity up to a maximum of about 75 J/g, the addition of the external modifier tends to decrease the MFR. An MFR as low as 0.3 g/ 10 min. may be obtained,

although the MFR is typically 0.4 g /10 min. to 60 g/ 10 min. in the FPO polymers. For example, one experiment with an Si:Ti molar ratio of 0.5:1, and an Al:Ti ratio of 200 (organometallic co-catalyst to pro-catalyst) yielded an MFR of about 3 g / 10 min., while an Si:Ti ratio of about 4:1 provided an MFR of about 0.3 g / 10 min.

The improved FPO polymers used as a component in the various blends according to this invention have a low crystallinity in the range of about 0.4 Joules per gram (J/g) to 75 J/g, although this may preferably range from about 4.6 J/g to 35 J/g or 15 J/g to 60 J/g. The polymers also have a melt flow rate of between about 0.4 g/ 10 min. to 60 g/ 10 min., and every whole integer therebetween. Preferably, the melt flow rate is between about 2.0 g/ 10 min. to 30 g/ 10 min. and every whole integer therebetween, more preferably between about 6.0 g / 10 min. to 20 g / 10 min., and every whole integer therebetween, and most preferably between about 8.0 g / 10 min. to 14.0 g / 10 min., and every whole integer therebetween.

While the blend components according to this invention may be prepared using continuous polymerization processes, they may, of course, also be prepared via batch polymerization. When used in continuous polymerization, the catalysts are typically dumped into the reactor in amounts sufficient to replace catalyst used. Polymerization of monomers to produce suitable core layer materials useful in the instant invention including propylene is typically conducted in a polymerization reactor with the catalysts of the invention in a liquid system with an inert diluent such as a paraffinic liquid of 3 to 15 carbon atoms per molecule, or in a liquid system containing propylene as sole diluent or together with a small amount of propane, or in vapor phase. Propylene polymerization in liquid phase is typically conducted at a temperature of about 40°C to 80°C, more preferably 50°C to 70°C, and most preferably 55°C to 65°C, at a pressure sufficient to maintain liquid conditions. Conventional operating conditions for propylene polymerization, other than the novel catalyst preparation and use taught herein, are well known to those skilled in the art and are not essential to the production of the polymers used as blend components in accordance hereto. In a continuous reaction system, the liquid

in the reaction zone is maintained at reaction conditions, monomer is continuously charged to the reaction zone, catalyst components are also charged continuously or at frequent intervals to the reaction zone, and reaction mixture containing polymer is withdrawn from the reaction zone continuously or at frequent intervals. For example, 660 mL of propylene batch polymerized with 10 mg of catalyst at 60°C for about 1 h provided a polymer having a H_f of about 27 J/g and an MFR of about 1.6 g / 10 min.

Polymer Characterization

It is common knowledge in the art that several different families of propylene-based polymers may be prepared in a polymerization reactor. Some examples of these polymer families include: isotactic propylene homopolymers, isotactic propylene/ethylene copolymers, amorphous poly- α -olefins ("APAO") propylene homopolymers, APAO propylene/ethylene copolymers, APAO propylene/butene copolymers. Through the instant invention the production of FPO propylene homopolymers, FPO propylene/ethylene copolymers, and FPO propylene/butene copolymers, inter alia, is now possible.

The FPO polymers produced in accordance hereto are typically propylene homopolymers, but they may also be copolymers of propylene formed from using a monomeric raw material feed comprising propylene in a mixture with at least one other monomeric material, such as a C_{2-12} alkene. The other monomeric raw materials are alpha-olefins in a preferred embodiment, such as ethylene, 1-butene, 1-pentene, and 1-octene. A particularly preferred component for use with propylene is ethylene, present preferably in about 1 to 20 weight percent of the polymer composition. Increasing the ethylene content inhibits the effects of the external donor to varying degrees, i.e., the increase in crystallinity of propylene domains within the polyolefin polymer otherwise seen.

The FPO polymers herein disclosed are characterized by a variety of properties, including the degree of crystallinity and the degree of polymerization. Crystallinity, or heat of fusion (ΔH_f) is typically measured by ASTM Method D-3417 (DSC). The

relative amounts of the catalyst components described in the catalyst system herein disclosed are capable of being adjusted to produce polymers having a heat of fusion that may range from about 0.4 J/g to 75 J/g, as is illustrated by the data set forth in the various tables. Preferably though, the desired range for purposes of blend component usage is in the range of about 5 J/g to 60 J/g, more preferably about 10 J/g to 30 J/g, and most preferably from about 12 to 25 J/g and a melt flow rate of between about 8.0 to 14 g / 10 min. (at 230°C).

MFR is measured according to ASTM-D1238 standard Method A/B (2.16 kg/230°C), such as on a Kayness Galaxy I Melt Indexer. The methyl ethyl ketone ("MEK") solution percent was determined by extracting about 5 g of polymer with 100 mL of boiling methyl ethyl ketone for 6 hours. Tensile tests (ASTM-D638) were performed on an Instron 1125 with Type I injection molded tensile bars at test speed of 2"/min. The VICAT softening point was measured in accordance with ASTM-D1525. Shore D hardness was determined in accordance with ASTM-D2240. Percent tensile set was measured after 300 percent extension and calculated by the following equation:

$$\% \text{ Tensile Set} = (L_f - L_i) / (L_n - L_i) \times 100\%$$

where L_i is the initial separation, L_n is the extension, and L_f is the final separation. A variety of other characteristics may be used to describe these polymers as well, such as VICAT softening point of about 40°C to 75°C, and preferably 45°C to 70°C; Shore D hardness of about 30 to 65, and more preferably about 40 to 55; tensile modulus; tensile stress; a melt swell ratio of about 1.6 or below, preferably about 1.5 or below, and most preferably about 1.4 or below. The VICAT softening point and Shore D hardness will vary depending on the melt flow rate, heat of fusion, and the like in the polymer product. The properties vary depending upon the specific FPO polymer produced, which is dependent upon the exact ratios of Al:Ti (co-catalyst to pro-catalyst) and Si:Ti (external modifier to pro-catalyst), as well as the specific silane or other similar compound used in the pro-catalyst and the external modifier. Thus, these polymers are defined primarily by means of their crystallinity, or heat of fusion, their melt flow rate, and

their molecular weight distribution, or polydispersity index ("MWD" or "PDI").

The molecular weight distribution, or polydispersity index, of the FPO polymers is about 10 or lower, preferably about 9 or lower, and most preferably about 8.5 or lower. The PDI is a ratio of the molecular weight average (M_w) over the molecular number average (M_n). The melt swell ratio is measured by the ratio of the diameter of a strand of extruded polymer to the diameter of the orifice through which it was extruded. A lower melt swell ratio is an indicator of a lower PDI, which itself indicates a narrower molecular weight distribution and, therefore, a less sticky, tacky, FPO polymer product. A low PDI combined with a low melt flow rate advantageously provides the polymers used as a core layer in the instant invention with desired characteristics. The low MFR of the FPO polymers tends to evidence a higher melt strength and higher viscosity, which vastly facilitates the production of such as tubing extrusions. A low methylethyl ketone-soluble fraction is characteristic of the reduced stickiness associated with the processing of the polymer, both during production and as a final product for consumer or industrial usage. For purposes of this invention, the words "reduced stickiness" mean a polymer comprising about 1 to 12 weight percent of an MEK-soluble fraction. The words "greatly reduced stickiness" mean a polymer comprising between about 2 to 5 weight percent of an MEK-soluble fraction.

Various additives may be included in the FPO polymers produced and used according to this invention, such as antioxidants, anti-block agents, slip additives, UV stabilizers, pigments, and the like. Adding or removing hydrogen during the polymerization described herein may affect the MFR of the FPO polymers, while having minimal impact on the degree of crystallinity.

EXAMPLES OF FPO PREPARATION

The polymers used in this invention are further defined by reference to the following examples describing in detail the preparation of the compounds and compositions useful therefor in the blend products disclosed. It will become apparent to those skilled in the art after reading this specification that many

modifications, both to materials and methods, may be implemented without departing from the spirit and utility of this invention.

A variety of catalysts for the preparation of FPO polymers were prepared and tested, and polymerization tests were conducted. Typical conditions included using liquid propylene in a 1.0 L stainless steel autoclave equipped with an agitator. After the reactor was thoroughly purged with nitrogen to remove any catalyst poisons, such as moisture and oxygen, 10 mg of solid pro-catalyst component were charged into the reactor as a 1 weight percent mixture in dry mineral oil, followed by addition of triethylaluminum co-catalyst in a prescribed amount to obtain an Al/Ti molar ratio of about 200:1. 300 g of liquid propylene were then charged into the reactor and the polymerization proceeded at 60°C for one hour under agitation sufficient to mix the components. At the end of the hour, the unreacted propylene was vented off and the polymer product was recovered. Properties of polymers prepared using various novel catalysts are set forth in the various tables included herein. In the examples, the "C-Donor" is cyclohexyl-methyl-dimethoxy-silane, and "D-Donor" is di-cyclopentyl-dimethoxy-silane.

A conventional catalyst may be prepared according to the disclosure of U.S. Patent No. 4,347,158. Example 1 of the '158 patent describes such a catalyst preparation as follows: Anhydrous $MgCl_2$ was prepared by drying at 350°C for 4 hours under an HCl blanket. 25 grams of this anhydrous $MgCl_2$, 4.34 g $AlCl_3$, and 7.01 g anisole were charged under nitrogen atmosphere into a vibrating ball mill having a 0.6 L capacity containing 316 stainless steel balls weighing a total of 3250 g and each having a diameter of 12 mm. This mixture was co-comminuted for 24 hours without temperature control. Titanium tetrachloride was precomplexed with ethyl benzoate (EB) in n-heptane at about 50°C. 6.19 g of this $TiCl_4$ EB complex was then charged into the vibrating ball mill after the prior 24 hour co-comminution of the other materials, and the resulting mixture co-comminuted for an additional 20 hours at ambient temperature and under inert atmosphere. This produced a solid catalyst component usable without requiring extraction or catalyst washing.

Another conventional catalyst was prepared, for comparison purposes with the catalysts of the present invention,

approximately as follows: 30 g (0.315 mole) of MgCl_2 was co-comminuted with 5.22 g (0.0391 mole) AlCl_3 for 24 h in RBM under N_2 atmosphere. Then 4.02 g (0.0212 mole) of TiCl_4 was added. Ball milling was continued for another 24 h. 30 g yellow pro-catalyst powder was collected. It was calculated that the titanium component was about 2.6 weight percent, the aluminum component was about 2.7 weight percent, the magnesium component was about 19.3 weight percent, and the Mg:Al:Ti ratio was about 8:1:0.5.

Examples 3-19 illustrate a variety of Type I donors and their effects on polymer properties. They were typically co-milled with catalyst supports ($\text{MgCl}_2/\text{AlCl}_3$) prior to TiCl_4 addition, except for the catalysts made by a solution process. The effect of the donors produced by the ball-mill method on productivity indicates silane donors are more effective than other donors in enhancing the productivity at low dosages. Those donors prepared by the solution process indicate a productivity enhancement that, with increasing donor dosage, also indicates an increased heat of fusion of the polymer. The desired donors are those that yield the maximum productivity increase while causing the minimum change to the heat of fusion. Silane donors advantageously meet the criteria most effectively.

Example 3: Same as Example 6 below, except using 1.18 g EtOBz. Calc'd: Ti%=2.50; EB/Mg=0.025 (mol/mol).

Example 4: MgCl_2 of 30 g, AlCl_3 of 5.25 g and EtOBz of 2.36 g (0.0158 mole) were ball milled (VBM) for 16 h, then TiCl_4 of 4.02 g was added and the mixture was ball milled for another 16 h. Calc'n: Ti%=2.43; EB/Mg=0.05 (mol/mol).

Example 5: Same as Example 6, except using 4.72 g EtOBz. Calc'd: Ti%=2.31; EB/Mg=0.10 (mol/mol).

Example 6: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 1.55 g (0.0131 mole) $(\text{EtO})\text{SiMe}_3$ and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 7: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 3.1 g (0.0263 mole) $(\text{EtO})\text{SiMe}_3$ and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 8: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 6.15 mL (0.0394 mole) $(\text{EtO})\text{SiMe}_3$ and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 9: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 2.47 g (0.0131 mole) C-donor and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 10: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 7.42 g (0.0394 mole) C-donor and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 11: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 3.0 g (0.0131 mole) D-donor and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 12: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 9.0 g (0.0394 mole) D-donor and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 13: 5 g of Example 2 was suspended in 100 mL toluene, stirred at 60°C for 1 h, filtered and suspended in 30 mL fresh toluene. 16.5 mL TiCl_4 and 0.74 mL (3.2 mmole) D-donor (Dicyclopentylmethoxysilane) were added. Mixture was stirred at 90°C for 1 h, filtered (solid dark brown), washed with heptane (turned to greenish yellow) and toluene (back to dark brown), again suspended in 30 mL toluene. 17 mL TiCl_4 was charged and mixture was stirred at 90°C for another 1 h. Solid filtered out and thoroughly washed with heptane.

Example 14: 1) MgCl_2 30 g, AlCl_3 5.25 g and $(\text{EtO})_3\text{SiMe}_3$ 7.02 g (0.0394 mole) were ball milled for 24 h. 2) 5 g of above precursor was suspended in 100 mL toluene, stirred at 60°C for 1 h, filtered, solid washed with heptane, toluene and then suspended in 30 mL fresh toluene. 16.5 mL (150 mmole) TiCl_4 was charged (slurry turned brown). The slurry was stirred at 90°C for 1 h, filtered, solid washed with heptane, toluene, then again suspended in 30 mL toluene. 16.5 mL TiCl_4 was charged and reacted at 90°C for 1 h. The solid was washed with heptane.

The solid was orange-red in toluene but turned to yellow after washed by heptane.

Example 15: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 6.69 g (0.0394 mole) SiCl_4 and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 16: 30 g MgCl_2 , 5.25 g AlCl_3 and 2.76 g dibutyl phthalate were co-ball milled for 24h, then 4.02 g TiCl_4 was added. The mixture was ball milled for another 24 h to provide the pro-catalyst.

Example 17: 30 g MgCl_2 and 2.76 g dibutyl phthalate were co-ball milled for 24h, then 4.02 g TiCl_4 was added. The mixture was ball milled for another 24 h to provide the pro-catalyst.

Example 18: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24h, then 7.68 g (0.0212 mole) diheptyl phthalate and 4.02 g (0.0212 mole) TiCl_4 were charged and ball milled for another 24 h.

Example 19: Same as Example 14 except without $(\text{EtO})_3\text{SiMe}$ but with dropwise addition of 1.17 mL diheptyl phthalate (turned dark) before reacting at 90°C for 1 h.

These pro-catalysts were used in a catalyst for the polymerization of polypropylene to produce polymers having characteristics set forth in the Tables.

A variety of catalysts were examined for Type II internal donor characteristics in an attempt to locate a catalyst that produces a smaller amount of the low molecular weight FPO polymers than typical.

Example 20: See Example 2.

Example 21: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 4.46 g (0.0394 mole) cis 2,6-dimethylpiperidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 22: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 5.56 g (0.0393 mole) 2,2,6,6-tetramethylpiperidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 23: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 4.19 mL (0.0394 mole) 2,5-

dimethylfurane and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 24: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 3.95 g (0.0394 mole) 2,5-dimethyltetrafurane and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 25: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 3.67 g (0.0394 mol) 2-picoline and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 26: 21.4 g MgCl_2 and 3.75 g AlCl_3 were ball milled (RBM) for 24 h, then 5.0 g (0.0281 mole) 4-chloroquinaldine and 2.85 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 27: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 4.59 mL (0.0394 mole) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 28: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 4.77 g (0.0393 mole) 2,4,6-collidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 29: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 5.0 g (0.0394 mole) 6-chloro-2-picoline and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 30: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 5.83 g (0.0393 mole) 2,6-dichloropyridine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 31: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 9.33 g (0.0394 mol) 2,6-dibromopyridine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example Number	Composition	Donor	Donor /Ti	Polymn. Run No	C. E. g/g-cat	ΔH_f J/g	m.p. °C	MFR g/10 min	MEK sol%
1	TiCl ₄ /MgCl ₂ /AlCl ₃ /EB/Anisole	EB & Anisole	nd	2507-39	11900	42.9	155.9	11	nd
7	TiCl ₄ /MgCl ₂ /AlCl ₃ (BM)	None	0	2536-1	16500	30	154	11	11
9	TiCl ₄ /MgCl ₂ /AlCl ₃ /EB (BM)	Ethyl Benzoate	0.37	2536-25	17600	31.8	153.8	10.3	12.5
4	TiCl ₄ /MgCl ₂ /AlCl ₃ /EB (BM)	Ethyl Benzoate	0.74	2536-21	16500	35.1	154.5	9.6	11.1
5	TiCl ₄ /MgCl ₂ /AlCl ₃ /EB (BM)	Ethyl Benzoate	1.48	2536-27	13800	39.2	154.7	7.4	12.2
6	TiCl ₄ /MgCl ₂ /AlCl ₃ /(EtO)SiMe ₃ (BM)	(EtO)Si Me ₃	0.62	2540-31	18800	36.1	153.9	8.4	10.4
7	TiCl ₄ /MgCl ₂ /AlCl ₃ /(EtO)SiMe ₃ (BM)	(EtO)Si Me ₃	1.24	2536-99	23300	35.1	153.5	8.9	7.6
8	TiCl ₄ /MgCl ₂ /AlCl ₃ /(EtO)SiMe ₃ (BM)	(EtO)Si Me ₃	1.86	2536-97	21000	43.9	152.4	15.3	7.8
9	TiCl ₄ /MgCl ₂ /AlCl ₃ /C-donor (BM)	C-donor	0.62	2540-7	19400	33.7	153.1	8.6	7.8
10	TiCl ₄ /MgCl ₂ /AlCl ₃ /C-donor (BM)	C-donor	1.86	2536-95	13400	40.9	152.8	7.5	5.5

Table I. - properties of examples 1 - 10

Example Number	Composition	Donor	Donor / Ti	Polymn. Run No	C.E. g/g-cat	ΔH_f J/g	m.p. °C	MFR g/10 min	MEK sol%
11	TiCl ₄ /MgCl ₂ /AlCl ₃ /D-donor (BM)	D-donor	0.62	2540-6	19800	35.9	153.7	9.9	5.7
12	TiCl ₄ /MgCl ₂ /AlCl ₃ /D-donor (BM)	D-donor	1.86	2536-93	13800	36.9	154.4	3.6	4.7
13	TiCl ₄ /MgCl ₂ /AlCl ₃ /D-donor (Solution)	D-donor	nd	2536-62	27300	37.7	154.2	12.7	9.4
14	TiCl ₄ /MgCl ₂ /AlCl ₃ /(EtO) ₃ SiMe (Solution)	(EtO) ₃ SiMe	nd	2536-54	18200	51.1	155.2	4.6	7.9
15	TiCl ₄ /MgCl ₂ /AlCl ₃ /SiCl ₄ (BM)	SiCl ₄	1.86	2536-91	13900	34.2	153.6	13.7	7.1
16	TiCl ₄ /MgCl ₂ /AlCl ₃ /D BP (BM)	Dibutyl Phthalate	0.47	2541-59	13900	46.9	156.0	4.2	8.4
17	TiCl ₄ /MgCl ₂ /DBP (BM)	Dibutyl Phthalate	0.47	2541-62	9900	44.2	155.4	4.0	8.4
18	TiCl ₄ /MgCl ₂ /AlCl ₃ /D HP (BM)	Diheptyl Phthalate	1	2536-58	10700	49.7	156.1	0.75	4.5
19	TiCl ₄ /MgCl ₂ /AlCl ₃ /D HP (Solution)	Diheptyl Phthalate	nd	2536-56	9700	49.7	156.7	1.2	7.1

nd = not determined

Polymerization conditions: 10 mg catalyst; 300 g propylene; Al/Ti=200; 60°C for 1 hour.

Table II. - Properties of Examples 11 - 19

Example No. ^a	Donor	Polymn Run No ^b	C.E. g/g-cat.h	ΔH_f J/g	M.P. °C	MFR g/10 min	MEK Sol%	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI
20	None	2536-1	16500	30	154	11	11	21	209	9.9
21	2,6-dimethylpiperidine	2536-79	7900	35.9	154.3	4.0	6.0	28	239	8.47
22	2,2,6,6-Tetramethylpiperidine	2540-51	7400	51.1	156.4	0.68	5.9	33	385	12.2
24	2,5-dimethylfuran	2536-76	14000	35.9	154.1	6.4	8.4	27	277	9.6
24	2,5-dimethyl-tetrahydrofuran	2536-80	13700	28.4	153.6	18.4	9.2	20	201	9.9
25	2-picoline	2540-84	13700	27.8	153.6	7.3	11.0	22	214	9.7
26	4-chloroquinoline	2536-86	6500	30.2	154.4	3.6	7.6	25	239	9.6
27	2,6-Lutidine	2536-68	6800	27.5	155.0	1.4	4.8	36	283	7.8
28	2,4,6-collidine	2540-37	9000	29.7	154.7	1.22	4.62			
29	6-chloro-2-picoline	2536-83	9300	27.8	154.5	1.2	3.8	36	280	7.8
30	2,6-dichloropyridine	2540-35	9100	26.9	154.4	3.1	8.1	32	265	8.29
31	2,6-dibromopyridine	2540-86	9300	27.6	153.6	2.1	8.9	29	295	10.3

a - Catalyst general composition: $TiCl_4/MgCl_2/AlCl_3/Donor$, ball milled. Donor/Ti = 1.86.

b - Polymerization conditions: 10 mg catalyst: Al/Ti=200: 60°C for 1 h.

Examples 20-31 illustrate a variety of Type II donors, including aromatic, sterically hindered nitrogen-based Lewis base donors. It was desired to obtain a higher molecular weight indicated by a lower MFR, while having a minimal effect on crystallinity. The results above suggest that: (1) the nitrogen-based donors are generally more effective in increasing molecular weight than oxygen-based donors (Examples 23 and 24, for example); (2) non-aromatic nitrogen-based Lewis bases, e.g., Examples 21 and 22, had a more pronounced effect on polymer heat of fusion than the aromatic derivatives, the latter being weaker Lewis bases; and (3) the steric hindrance around the nitrogen atom importantly appears to increase steric hindrance from 2-picoline to 2,6-lutidine to 2,6-dibromopyridine, with the low molecular weight fractions first decreased, then increased again. 2,6-lutidine and 6-chloro-2-picoline were more effective in reducing the LMW fractions. A variety of catalysts were prepared and tested to obtain a good

productivity, while yielding higher molecular weight and lower crystallinity:

Example 32: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 5 h, 1.55 g (0.0131 mole) $(\text{EtO})\text{SiMe}_3$ was added and ball milled for 19 h, then 4.22 g (0.0394 mole) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 33: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 hrs., then 3.1 g (0.026 mole) $(\text{EtO})\text{SiMe}_3$ and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 hrs. 10 g of this mixture were suspended in 30 mL toluene, to which 33 mL TiCl_4 and 0.75 mL (0.0064 mole) 2,6-Lutidine were added. The mixture was stirred at 90°C for 1 h, then filtered (filtrate orange) and washed with heptane for 3 times to give the yellow pro-catalyst.

Example 34: 30 g MgCl_2 , 5.25 g AlCl_3 and 0.74 g diethoxydimethylsilane were co-ball milled for 24 h, then 1.41 g 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 35: 30 g MgCl_2 , 5.25 g AlCl_3 and 0.95 g C-donor were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 36: 30 g MgCl_2 , 5.25 g AlCl_3 and 1.23 g dicyclopentylmethoxysilane were ball milled for 24 h, then 1.41 g 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 37: 30 g MgCl_2 , 5.25 g AlCl_3 and 1.38 dibutyl phthalate were ball milled for 24 h, then 1.41 g 2,6-lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 38: 30 g MgCl_2 , 5.25 g AlCl_3 and 0.95 g C-donor were ball milled (RBM) for 24 h, then 1.66 g (0.0131 mol) 6-chloro-2-picoline and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 39: 30 g MgCl_2 , 5.25 g AlCl_3 and 0.95 g C-donor were ball milled (RBM) for 24 h, then 3.32 g (0.0262 mol) 6-chloro-2-picoline and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 40: 5 g of the pro-catalyst in Example 2 was suspended in 100 mL toluene and stirred at 60°C for 1 h. The solid was filtered out and re-suspended in 30 mL toluene. 16.5 mL TiCl_4 and 0.1 mL (0.0005 mole) C-donor were added into the suspension. The mixture was then stirred at 90°C for 1 h, filtered and washed with heptane then toluene. The solid was re-suspended in 30 mL toluene and mixed with 16.5 mL TiCl_4 and 0.41 g (0.0032 mole) 6-chloro-2-picoline. The mixture was brought to reaction at 90° for another hour, then filtered and washed with heptane for 3 times to give the pro-catalyst.

Example 41: 5 g of the pro-catalyst in Example 2 was suspended in 100 mL toluene and stirred at 60°C for 1 h. The solid was filtered out and re-suspended in 30 mL toluene. 16.5 mL TiCl_4 and 0.25 mL (0.001 mole) D-donor were added into the suspension. The mixture was then stirred at 90°C for 1 h, filtered and washed with heptane twice. The solid was re-suspended in 30 mL toluene and mixed with 16.5 mL TiCl_4 and 0.41 g (0.0032 mole) 6-chloro-2-picoline. The mixture was brought to reaction at 90° for another hour, then filtered and washed with heptane for 3 times to give the pro-catalyst.

Example 42: 5 g of the pro-catalyst in Example 2 was suspended in 100 mL toluene and stirred at 60°C for 1 h. The solid was filtered out and re-suspended in 30 mL toluene. 16.5 mL TiCl_4 and 0.1 mL (0.0004 mole) D-donor were added into the suspension. The mixture was then stirred at 90°C for 1 h, filtered and washed with heptane then toluene. The solid was re-suspended in 30 mL toluene and mixed with 16.5 mL TiCl_4 and 0.41 g (0.0032 mole) 6-chloro-2-picoline. The mixture was brought to reaction at 90° for another hour, then filtered and washed with heptane for 3 times to give the pro-catalyst.

Example 43: 30 mg MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 hrs., then 1.55 g (0.013 mole) $(\text{EtO})\text{SiMe}_3$ and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 hrs. 5 g of this mixture was suspended in 100 mL toluene and stirred at 80°C for 1 h. The solid was filtered out and re-suspended in 30 mL toluene. 16.5 mL TiCl_4 and 0.41 g (0.0032 mole) 6-chloro-2-picoline were added into the suspension. The mixture was then stirred at 90°C for 1 h, filtered and washed with heptane for three times to give the pro-catalyst.

Example 44: 5 g of the mixture of Example 43 was suspended in 100 mL toluene and stirred at 80°C for 1 h. The solid was filtered out and re-suspended in 30 mL toluene. 16.5 mL TiCl₄ and 0.0032 mole 2,6-dichloropyridine (dissolved in toluene) were added into the suspension. The mixture was then stirred at 90°C for 1 h, filtered and washed with heptane for three times to give the pro-catalyst.

Example Number	A-type Donor (Donor/Ti)	B-type Donor (Donor/Ti)	Polymn. Run No	C.E. g/g-cat.h	ΔH_f J/g	M.P. °C	MFR g/10 min	MEK Sol %
32 (BM)	(EtO)SiMe ₃ Si/Ti=0.62	2,6-Lutidine N/Ti=1.86	2540-24	4500	36.8	153.5	1.2	7.1
33 (solution)	(EtO)SiMe ₃ Si/Ti nd	2,6-Lutidine N/Ti nd	2540-39	10900	42.6	155.3	1.3	4.4
34 (BM)	(EtO) ₂ SiMe ₂ Si/Ti=0.23	2,6-Lutidine N/Ti=0.62	2541-53	14300	36.6	154.2	1.9	7.2
35 (BM)	C-donor Si/Ti=0.23	2,6-Lutidine N/Ti=0.62	2540-91	15500	28.3	152.9	1.6	8.0
36 (BM)	D-donor Si/Ti=0.23	2,6-Lutidine N/Ti=0.62	2541-51	14000	38.3	154.5	1.3	5.3
37 (BM)	Dibutyl phthalate DBP/Ti=0.23	2,6-Lutidine N/Ti=0.62	2541-23	10500	32.9	154.5	nd	7.4
38 (BM)	C-donor Si/Ti=0.23	6-chloro-2-picoline N/Ti=0.62	2540-96	14700	29.6	153.7	3.1	7.4
39 (BM)	C-donor Si/Ti=0.23	6-chloro-2-picoline N/Ti=1.24	2540-98	10500	27.8	153.8	1.2	7.0
40 (solution)	C-donor Si/Ti n.d.	6-chloro-2-picoline N/Ti n.d.	2540-77	9300	26.7	154.1	1.0	6.5
41 (solution)	D-donor Si/Ti n.d.	6-chloro-2-picoline N/Ti n.d.	2540-53	15700	29.7	153.3	1.8	5.7
42 (solution)	D-donor Si/Ti n.d.	6-chloro-2-picoline N/Ti n.d.	2540-67	9700	28.1	155.0	1.7	5.7
43 (solution)	(EtO)SiMe ₃ Si/Ti n.d.	6-chloro-2-picoline N/Ti n.d.	2540-47	8300	35.7	155.4	1.0	6.8
44 (solution)	(EtO)SiMe ₃ Si/Ti n.d.	2,6-dichloropyridine N/Ti n.d.	2540-49	19100	36.1	154.1	4.2	6.9

BM = ball milling

Table IV.

The goal of Examples 32-44 was to obtain a catalyst with good productivity, while yielding higher molecular weight and lower crystallinity. Examples 32-44 illustrate the combinations of these donors by both ball mill and solution process. It appeared that the most promising combinations are those between C-donor, D-donor and 2,6-Lutidine, 6-chloro-2-picoline. D-donor and 2,6-Lutidine seemed to cause slightly higher heat of fusion. Also, the solution process appeared less advantageous as compared to the ball mill process.

Likely candidates for catalysts having all desired properties were selected to optimize all characteristics in the catalyst and resulting FPO polymer:

Example 45: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 4.59 mL (0.0394 mole) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 46: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 2.81 g (0.0262 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 47: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 48: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 0.74 g (0.0069 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 49: 30 g MgCl_2 and 5.25 g AlCl_3 were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 8.04 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 50: 30 g MgCl_2 , 5.25 g AlCl_3 and 0.95 g C-donor were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 8.04 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 51: 30 g MgCl_2 , 5.25 g AlCl_3 , and 0.48 g C-donor were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 52: 30 g MgCl_2 , 5.25 g AlCl_3 , and 0.95 g C-donor were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example 53: 30 g MgCl_2 , 5.25 g AlCl_3 , and 1.43 g C-donor were ball milled (RBM) for 24 h, then 1.41 g (0.0131 mol) 2,6-Lutidine and 4.02 g TiCl_4 were added. The mixture was ball milled for another 24 h to give the pro-catalyst.

Example No.	Ti %	C-donor (Si/Ti)	2,6-Lutidine (N/Ti)	Polymn. Run No	C.E. g/g-cat.h	ΔH_f J/g	M.P. °C	MFR g/10 min	MEK Sol%	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI
45	2.33	0	1.86	2540-1	6400	31.8	154.8	1.5	6.8	36	283	7.78
46	2.41	0	1.24	2540-71	8800	27.4	154.2	1.6	7.2	40	299	7.45
47	2.50	0	0.62	2540-75	12700	27.3	153.4	1.9	6.9	32	273	8.4
48	2.54	0	0.32	2540-82	15900	29.5	152.6	3.2	10.1	26	247	9.41
49	4.54	0	0.31	2540-80	12600	32.7	154.6	1.9	6.6	31	242	7.74
50	4.47	0.118	0.31	2540-89	15100	38.8	154.0	2.4	5.5	36	263	7.37
51	2.47	0.118	0.62	2541-6	14300	29.5	153.6	2.3	8.0			
52	2.44	0.23	0.62	2540-91	15500	28.3	152.9	1.6	8.0	32	274	8.48
53	2.41	0.35	0.62	2541-8	15000	37.1	153.5	1.8	5.9			

Table V.

Examples 45-53 illustrate the optimization of donor dosage by locating a point where the MFR is sufficiently low, but catalyst productivity is acceptably high for polymerization, as well as the optimization of maintaining improved productivity while obtaining low heat of fusion. Example 52 appears as the pro-catalyst advantageously having the optimum recipe, with a relatively high productivity of 15,500 g/ g catalyst, relatively low H_f of about 28.3 J/g, and significantly lower MFR of about 1.6 g / 10 min. than for other catalyst formulations.

EXAMPLE 54 - preferred catalyst 120 lbs. of solid magnesium chloride ("MgCl₂") and 21 lbs. of solid aluminum chloride ("AlCl₃") were charged to a 250 L vibratory ball mill and mixed for about 15 minutes. Then, 3.8 lbs. of cyclohexylmethyldimethoxysilane was sprayed into the stainless steel container. The mixture was then ball milled for 16 hours at room temperature. Subsequent to the initial ball milling, 3.7 lbs. of liquid 2,6-lutidine and 16.1 lbs. of liquid titanium tetrachloride (TiCl₄) were added to the mixture. An alternative heterocyclic aromatic amine, such as about 4.5 lbs. of liquid 6-chloro-2-picoline could instead have been substituted. The lutidine was directly added to these components. The five (5) components were then ball milled for about an additional 16 hours. The ball milling involves vibrating steel balls to pound the component particles, imparting heat to the ball milling vessel;

however, the vessel was equipped with a heat-exchanger to maintain approximately room temperature during the ball milling.

In the preparation of a variety of FPO polymers, the productivity of the present catalyst has ranged from about a 30 to 55 percent increase, compared to conventional catalysts.

Examples 55-62 - pilot plant continuous process - Polymers were prepared in a large scale continuous pilot plant operation, wherein monomers, hydrogen, and catalyst components were separately and continuously charged to a stirred reactor. The total monomer feed rate corresponded to about a 1.8 hour residence time in the reactor. Triethylaluminum ("TEA") and external modifier cyclohexylmethyldimethoxysilane ("CMDs") were pumped into the reactor as about 5 weight percent and 0.25 weight percent heptane solutions, respectively. The solid catalyst component had a titanium content of about 2.2 weight percent and was prepared according to Example 54. The solid catalyst component was pumped into the reactor as a 25 weight percent mixture in petrolatum. The catalyst components were added at rates directly proportional to the polymer production rates, and in amounts sufficient to maintain the polymer solids concentration in the reactor slurry at values typically in the range of about 30 to 50 weight percent. The catalyst productivity (lbs polymer/lb solid catalyst) was calculated from the polymer solids withdrawal rate and the solid catalyst component addition rate. The product polymers were separated from unreacted monomers, deactivated, stabilized, and pelletized, followed by testing to determine polymer characteristics. Table VI. summarizes the pertinent operating conditions and results of the physical testing of the polymer characteristics.

Example	55	56	57	58	59	60	61	62
Reactor Temp °F	135	135	135	135	135	135	140	140
Propylene (lbs/hr)	138	154	136	146	142	147	147	135
Ethylene (lbs/hr)	-	-	1.5	1.1	-	-	-	-
Hydrogen (lbs/hr)	-	0.028	-	0.028	0.026	0.040	0.027	0.04
Solid catalyst (lbs/hr)	0.0045	0.0038	0.0029	0.0026	0.0045	0.0048	0.0055	0.0046
Al/Ti mol ratio	162	210	256	364	155	184	161	191
CMDS/Ti mol ratio	-	-	-	-	0.77	0.87	2	-
Productivity (lbs/hr)	9880	11600	16110	16890	9630	10420	8480	10090
Ethylene - wt %	-	-	2.2	2.6	-	-	-	-
ΔH_f (J/g)	26.6	23.8	17.8	18.2	33.5	36.1	50.4	53.4
MFR (g / 10 min)	4.6	13.6	4.9	15.8	7.4	30	4.8	25.9
Tensile Modulus (kpsi)	11	9	-	3	20	20	40	43
Tensile stress @ 311% strain - psi	1330	935	983	660	1400	1087	2100	1720
% Tensile set. 0/24 hr	36/23	34/19	31/17	30/17	46/31	45/29	63/45	69/50
VICAT softening (°C)	58	46	41	42	66	57	95	97
Shore D Hardness	46	45	38	34	51	50	61	62

Table VI.

The polymerization of several polymers, which are by no means indicative of the broad scope of polymers this invention is meant to encompass, was examined using the ball-milled catalyst of the present invention. The characteristics of some of these polymers are set forth in Table VII:

Example No.	63	64	65	66	67	68	69	70	71
Pro-cat., mg	10	10	10	10	10	10	10	10	10
Co-catalyst	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA	TEA
Al/Ti, mol/mol	200	200	200	200	200	200	200	200	200
Modifier		CMDS		CMDS					
Modifier/Ti, mol/mol		1		1					
H ₂ , psig	0	0	5	5	0	0	0	0	0
Ethylene, g/min ^{a)}	0	0	0	0	0.27	0	0	0	0
Propylene mL	660	660	660	660	660	610	460	610	460
1-butene, mL	0	0	0	0	0	50	200	0	0
1-pentene, mL	0	0	0	0	0	0	0	50	200
C.E. g/g cat/h	15300	10400	17500	13100	19600	11000	10600	9400	8000
H.F., J/g	32.2	57.2	34.8	62.7	25.6	21.8	13.8	21.9	6.6
m.p., °C	153.7	156.4	155.9	158.3	146.7	137.3	109.7	141.0	126.9
MFR, g/10 min	2.16	0.3	12.0	21.9	2.24	4.1	6.3	4.4	10.2

Batch polymerization in 1 liter autoclave, 60°C, for 1 hr.
a) Ethylene continuously fed during 1 hour reaction time.

Table VII.

Each of the polymer products in Examples 72 to 83 set forth in Table VII were prepared in general by the process described in the Examples above. These materials are copolymers of propylene with other monomers including 1-butene, 1-pentene, and 1-octene. Initially, a clean one-liter stainless steel autoclave reactor equipped with an agitator was purged with nitrogen to remove impurities. Next, triethylaluminum is added to the reactor in sufficient quantity to provide an Al:Ti atomic ratio of about 200:1 when followed by addition of a mineral oil suspension containing about 10 mg of solid procatalyst as described herein. The mixed monomer charges, which include 660 mL liquid volume, were subsequently introduced into the reactor at an effective pressure and under thermal control to maintain a reaction temperature of 60°C for one hour. The "C" and "D" donors were those used previously. After one hour, the unreacted monomer was vented off and the polymer product was recovered using conventional techniques.

Ex. No.	72	73	74	75	76	77	78	79	80	81	82	83
Propene (mL)	640	610	560	460	640	610	560	460	640	610	560	460
1-butene (mL)	20	50	100	200	0	0	0	0	0	0	0	0
1-pentene (mL)	0	0	0	0	20	50	100	200	0	0	0	0
1-octene (mL)	0	0	0	0	0	0	0	0	20	50	100	200
C.E. g/g-cat/hour	13200	11000	10600	10700	13000	10400	10300	8000	12600	12200	12300	11000
wt% C ₄ -s	1.8	5.9	11.4	28.7	3.5	4.2	8.9	26.4	1.2	3.0	8.5	13.8
\overline{M}_n^a	69.7	21.8	11.3	4.6	65.7	39.8	19.5	8.0	186.2	84.7	32.7	17.4
\overline{M}_w^b	-	1.1	1.1	1.4	-	-	1.1	1.6	-	-	-	1.1
H.F. J/g	28.3	25.4	18.3	7.4	23.9	18.4	16.9	10.4	26.2	24.0	19.9	14.3
m.p. °C	149.0	136.6	131.6	110.1	146.5	139.9	132.5	130.0	150.5	147.2	144.2	146.4
T _g , °C	-1.5	-3.0	-5.1	-9.8	-2.1	-3.4	-3.9	-6.8	-2.8	-3.0	-5.6	-11.9
MFR. g/10 min.	3.2	4.0	2.8	6.6	3.8	5.0	6.8	10.2	2.9	3.8	5.3	8.9
Density g/cm ³	0.873	0.865	0.869	0.864	0.871	0.868	0.866	0.856	0.87	0.874	0.866	0.863
MEK solt	8.1	6.8	5.2	4.6	8.0	7.2	8.2	6.1	7.6	8.1	7.4	7.1

Batch polymerization in 1 liter autoclave. Catalyst 10 mg; TEA/Ti 200; Total liquid monomer charge 660 mL; 60°C; 1 hr.

- a) Weight percentage of co-monomer incorporation.
- b) Number average sequence length for propylene units.
- c) Number average sequence length for co-monomer units.

Table VIII.

The physical properties of polymers produced according to the present invention by using relatively higher percentages of ethylene as a component of the monomeric raw material mixture comprising propylene are set forth in table IX as Examples 84 - 93.

Values in the Enthalpy column in the various charts are shown as a positive and negative energy value since one value is for the heat of fusion and the other is for the heat of crystallinity.

HIGHER ETHYLENE FPO PRODUCTS

EXAMPLE NO.	84	85	86	87	88	89	90	91	92	93
LOT Melt Flow, g/10min@230°C	5.3	5	5.8	5.7	5.5	5.3	4.7	5	5.5	5.2
Ethylene Content, wt%	2.2	3.8	5.7	7.3	9.7	9.6	14.8	17.7	15	16.6
DSC M_f/F_d (°C)	147.2/9 3.8	144.5/92.2	136.6/88 .1	132.0/85 .3	127.6/84 .4	127.9/84 .5	123.3/ 80.9	118.9/77.6	120.5 /77.7	114.9 /73.5
Enthalpy (J/g)	17.5/21 .6	14/-19.7	14.1/- 13.1	11.5/- 12.6	7.9/- 10.6	8.1/-9.6	5.7/- 7.7	4/-4.4	5.2/- 6.8	4.5/- 4.9
Density, g/cm ³	—	—	0.8683	—	—	0.8597	—	0.8446	—	—
DSC T_g , °C	—	-6.7	-9.3	-16.2	—	-17.7	-24.1	-26.1	—	—
MEK Solubles, wt%	9.03	9.42	7.89	7.67	7.07	6.77	6.8	7.2	—	—
Diethyl Ether Sol., wt.	31.5	35.9	41.5	45.2	47	45.5	48.2	47.4	—	—
Hexane Sol. wt%	39.5	45.6	51.8	62.6	70.5	68.6	77.3	81.6	80.6	82.3
Shore Hardness, A/D scales	377-	337-	28/85	25/81	20/75	20/76	15/67	12/61	15/66	12/62
Shrinkage Test:										
Length (in/in)	—	0.0363	—	—	—	0.0669		0.0838	—	—
Width (in/in)	—	0.0016	—	—	—	-0.0078		-0.0065	—	—
Molecular Weight Measures:										
GPC Mn(x100 0)	27	26	27	27	27	27	27	28	32	27
Mw(x100 0)	219	221	222	224	222	226	218	207	219	203
Mz(x100 0)	792	836	873	889	905	916	968	850	857	821
PDI	8.1	8.5	8.22	8.3	8.22	8.4	8.1	7.4	6.8	7.5
I.V. of neat polymer, dl/g	1.48	1.96	1.24	1.63	1.25	1.67	1.37	1.23	—	—
I.V. of ether soluble fraction, dl/g	0.826	0.87	0.61	0.82	0.87	0.79	0.8	0.91	—	—
Cast Tubing 1 mil by 6 inches:										
Measured Thickness (mil)	1.6-2.1	—	1.6-1.7	—	—	1.3	—	1.7-1.8	—	—
Machine Direction:										
Stress @ Yield (psi)	733	—	NY	—	—	NY	—	NY	—	—
Stress @ Break (psi)	1761	—	1468	—	—	1052	—	870	—	—
Strain @ Break (%)	549	—	568	—	—	415	—	656	—	—

EXAMPLE NO.	84	85	86	87	88	89	90	91	92	93
Transverse Direction:										
Stress @ Yield (psi)	539	—	401	—	—	NY	—	NY	—	—
Stress @ Break (psi)	NB(989)	—	NB(728)	—	—	NB(516)	—	NB(226)	—	—
Strain @ Break (%)	NB(> 700)	—	NB(> 700)	—	—	NB(> 700)	—	NB(> 700)	—	—
Tensile Modulus (kpsi)	5.1	3.8	2.6	2.2	1.6	1.6	1.2	0.87	1.11	0.88
Tensile Strain at Yield (%)	NY	NY	NY	NY	NY	NY	NY	NY	NY	NY
Tensile Strain at Yield (psi)	NY	NY	NY	NY	NY	NY	NY	NY	NY	NY
Tensile Strain at Break (%)	NB	NB	NB	NB	NB	NB	NB	NB	NB	NB
Tensile Strain at Break (psi)	NB	NB	NB	NB	NB	NB	NB	NB	NB	NB
Tensile Strain at Max. Stain (311%) (psi)	936	844	699	626	550	547	359	270	354	291
Tensile Set after 300% Extension (%) (0/24h)	31/16	30/17	30/15	29/15	29/13	29/13	35/13	38/13	36/14	36/13
VICAT Softening Temperature (°C)	40	40	40	39	43	43	23	23	23	23
Melt Swell Ratio (210°C/5 kg)	1.502	1.52	1.55	1.566	1.524	1.536	1.486	1.49	1.498	1.46
Zero-Shear Viscosity (Pa-s)	9675	8823	8312	8796	8456	8624	8713	7945	7984	7740
Crossover Modulus (Pa)	22044	22277	22461	22800	24509	24638	29304	31881	29641	30252
PDI = 100,000/Gc	4.54	4.49	4.45	4.38	4.08	4.06	3.41	3.14	3.37	3.31
Crossover Frequency, rad/s	21.09	23.2	25.6	25.13	27.75	27.99	34.04	40.21	37.17	39.79

Table IX (cont.) - Properties of Examples 84 - 93

HIGHER ETHYLENE FPO PRODUCTS WITH DONOR ADDED

EXAMPLE NO.	94	95	96	97	98	99
LOT Melt Flow, g / 10 min. @ 230°C	5.5	8.4	4	4.8	5.6	6.9
Ethylene Content, wt%	9.7	6.2	14.7	12.6	9.8	9.8
DSC M _g /F _g (°C)	132.2/86.6	136.3/93/1	121.9/81.1	126/84.6	130.8/88.8	130.8/87.5
Enthalpy (J/g)	27.3/-30.7	23/-24.7	14.6/-19.4	17.8/20.3	21/-18.9	29.4/-30.7
Density, g/cm ³	—	—	—	—	0.874	0.878
MEK Solubles, wt%	4.96	6.31	3.4	—	—	—
Diethyl Ether Sol., wt%	23	27.7	29.5	—	—	—
Shrinkage Test:						
Length(in/in)	—	0.0125	0.0181	—	0.0133	0.0125
Width(in/in)	—	0.0137	0.0143	—	0.0133	0.0136
I.V. of neat polymer, dl/g	1.9	1.3	1.65	—	—	—
I.V. of ether soluble fraction, dl/g	0.57	0.37	0.8	—	—	—
Cast Tubing 1 mil by 6 inches:						
Measured Thickness(mil)	1.4-1.5	1.4-1.7	1.4-1.5	—	—	—
Machine Direction			711	—	—	—
Stress @ Yield(psi)	1047	959	1356	—	—	—
Stress @ Break(psi)	2760	2043	552	—	—	—
Strain @ Break(%)	538	653	—	—	—	—
Transverse Direction						
Stress @ Yield(psi)	733	774	566	—	—	—
Stress @ Break(psi)	NB(1500)	NB(1510)	NB(1190)	—	—	—
Strain @ Break(%)	NB	NB	NB	—	—	—

Table X.(cont.) - Properties of Examples

The instant invention contemplates the use as blend components of all polymeric FPO materials previously described herein which are made using the novel catalyst material also disclosed. The breadth of this invention is appreciated when it is considered that the novel FPO material(s) may be combined or blended with a multitude of prior art materials in order to arrive at novel and useful blend formulations suitable for use in various applications.

The discovery of the catalyst materials herein disclosed has made possible a multitude of possible new blend formulations. The best mode of this invention thus far seen by the inventors hereof has been the one in which the blend contains between about 5 % to 95 % of added FPO polymers produced in accordance hereto. More preferably the blends contain between about 10 % and 50 % of FPO polymers, and most preferably the blends contain between about 20 % and 40% of FPO polymers produced in accordance with the various Examples herein set forth. Most preferably, the FPO content is 33%.

Another type of catalysts for olefin polymerization known as "metallocenes" have come into widespread usage in recent years. Generally speaking, metallocene catalysts comprise a transition metal atom, typically zirconium, hafnium, vanadium, or titanium which has at least one cyclopentadienyl ligand pi-bonded to it. Often the transition metal atom is positioned between two cyclopentadienyl ligands wherein the metal atom is said to be "sandwiched" between the two ligands. The famous compound known as ferrocene, discovered by Wilkinson is exemplary of such an arrangement.

In the field of olefin polymerization catalysis, much creative work has also been undertaken with regard to modification of the basic structure of ferrocene. Replacement of the iron atom by one of the aforesaid transition metals has provided a basic framework for investigators to modify with the hopes of producing polymers having hitherto unbeknownst beneficial physical properties. By substituting various organic and inorganic moieties in the position of the hydrogen atoms of the basic framework, a multitude of compounds useful in olefin polymerization have been discovered, with nearly each having its own unique effect on polymers produced using it as a catalyst. Examples of US patents which have been generated as a result of these types of modifications to the basic

framework include: 5,594,080 ; 4,769,510 ; 4,808,561 ; 4,871,705 ; 4,935,397 ; 5,578,690 ; 5,132,262 ; 5,208,357 ; 5,232,993 ; 5,280,074 ; 5,314,973 ; 5,322,902 ; 5,349,100 ; 5,496,781 ; 5,525,690 ; 5,585,508 ; 5,631,202 ; 5,637,744 ; 5,329,033 ; 5,243,001 ; 5,241,025 ; 5,278,264 ; 5,227,440 ; 5,214,173 ; 5,162,466 ; 5,145,819 ; 5,120,867 ; 5,103,030 ; 5,084,534 ; 5,064,802 ; 5,057,475 ; 5,055,438 ; 5,017,714 ; 5,008,228 ; 4,937,299 ; 5,081,322 ; and 5,036,034 , the entire contents of which, including patents and publications referenced therein, are herein incorporated by reference. It will be appreciated by those skilled in the art of this invention that various polymeric products mentioned earlier produced using metallocene catalysts are just as useful as materials from which the blends of a this invention may be comprised, and the suitability for use of such materials is readily determinable without undue experimentation by one of ordinary skill. That is, it is not a critical factor for purposes of producing the blends in accordance hereto whether a given polypropylene for example, which is mixed with the PFO polymers of this invention, is produced using either Ziegler / Natta type or metallocene type catalysts.

In order to produce the blends of this invention, illustrated in examples 100 - 125 one provides the various components, preferably in their pelletized form and causes the materials to be effectively mixed with one another. A method for achieving this is to first mix the pellets of different materials in the dry state in a tumbling chamber in which the pellets are repeatedly agitated by virtue of rotation of the chamber in which they are contained about an axis perpendicular to the forces of gravity for sufficient time to effect a good mix. The mixture may also contain as additives other materials deemed desirable for the application at hand, as the use of such additives including slip additives, anti-block additives, anti-oxidants, colorants, and the like are well-known to those of ordinary skill in the art. Once the components have been well-mixed in the dry state, they are then fed into the throat portion of an extruder, such as the Haake Model TW-100, in which the materials are co-melted with one another, fed through the extruder via a mono screw or plurality of screws and forced through a die equipped with a cutter whereby pellets of homogeneous polymer blend compositions according to this invention emerge. The

following examples are embodiments of this invention disclosed for purposes of exemplifying the versatility of the uses which the novel polymers produced hereby exhibit, and can not be properly construed as being delimitive of the scope of the invention.

By the examples herein set forth, it is readily observed that by altering the relative amounts of catalyst components and reaction conditions, a wide range of FPO polymer products may be produced. The following tables are illustrative of some of the products now commercially available from Huntsman Polymers Corporation and which are properly classifiable as FPO polymers for purposes of the instant invention.

Example 100

Twenty pounds of "Affinity"(TM) EG 8150 available from Dow Chemical Company, Midland, Michigan are blended as described above with 80 pounds of an FPO polymer produced in accordance with example 88. (Such a polymer is known as "W209" and is available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 101 - thermoplastic resin

Twenty pounds of "Affinity"(TM) SM 1250" available from Dow Chemical Company, Midland, Michigan are blended as described above with 80 pounds of an FPO polymer produced in accordance with example 88. (Such a polymer is known as "W209" and is available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 102 - thermoplastic resin

Eighty pounds of "Engage 8180" (TM) thermoplastic elastomer available from DuPont Dow Elastomers is blended with 20 pounds of FPO homopolymer "W201", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 103 - thermoplastic elastomer

Eighty pounds of "Engage 8200" (TM) thermoplastic elastomer available from DuPont Dow Elastomers is blended with 20 pounds of FPO homopolymer "W202", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 104 - thermoplastic elastomer

Eighty pounds of "Engage 8400" (TM) thermoplastic elastomer available from DuPont Dow Elastomers is blended with 20 pounds of FPO homopolymer "W202", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 105 - thermoplastic elastomer

Eighty pounds of "Engage 8403" (TM) thermoplastic elastomer available from DuPont Dow Elastomers is blended with 20 pounds of FPO homopolymer "W204", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 106 - thermoplastic elastomer

Eighty pounds of "Engage 8445" (TM) thermoplastic elastomer available from DuPont Dow Elastomers is blended with 20 pounds of FPO homopolymer "W203", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 107 - thermoplastic elastomer

Eighty pounds of FPO homopolymer "W202", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas) is blended with 20 pounds of "Engage 8200" (TM) thermoplastic elastomer available from DuPont Dow Elastomers to produce a thermoplastic blend of enhanced flexibility.

Example 108 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 101-55 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 109 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 101-64 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 110 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 101-87 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 111 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 103-50 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 112 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 111-45 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 113 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 111-80 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 114 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) 211-87 from AES is blended with 30 pounds of FPO propylene copolymer from example 88 containing about 10 % ethylene, known as "W209", available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 115 - thermoplastic vulcanizate

Eighty pounds of Santoprene (TM) grade 211-55 are combined as described above with 20 pounds of an FPO polymer produced in accordance with example 57.

Example 116 - ethylene/acrylic acid copolymer

Twenty pounds of "Primacor"(TM) 1320" available from Dow Chemical Company, Midland, Michigan are blended as described above with 80 pounds of an FPO polymer produced in accordance with example 88. (Such a polymer is known as "W209" and is available

from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 117 - ethylene/acrylic acid copolymer

Twenty pounds of "Primacor"(TM) 1410-XT available from Dow Chemical Company, Midland, Michigan are blended as described above with 80 pounds of an FPO homopolymer known as "W202" available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 118 - ethylene/acrylic acid copolymer

Eighty pounds of "Primacor"(TM) 1420 available from Dow Chemical Company, Midland, Michigan are blended as described above with 20 pounds of an FPO homopolymer known as "W202" available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas).

Example 119 - polyester elastomer

Eighty pounds of Hytrel 4774 available from DuPont Engineering Polymers, 713 Chestnut Run Plaza, Wilmington, Delaware, are blended as described above with 20 pounds of an FPO homopolymer known as "W202" (available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas) which has been graft polymerized with maleic acid anhydride to contain about 9 % maleic anhydride.

Example 120 - polyester elastomer

Eighty pounds of Hytrel HTR8068 available from DuPont Engineering Polymers, 713 Chestnut Run Plaza, Wilmington, Delaware, are blended as described above with 30 pounds of an FPO copolymer known as "W209" (available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas) which has been graft polymerized with maleic acid anhydride to contain about 8 % maleic anhydride.

Example 121 - polyester elastomer

Eighty pounds of Hytrel 7246 available from DuPont Engineering Polymers, 713 Chestnut Run Plaza, Wilmington, Delaware, are blended as described above with 30 pounds of an FPO copolymer known as "W209" (available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas) which was previously graft polymerized with maleic acid anhydride to contain about 11 % maleic anhydride.

Example 122 - polyester elastomer

Eighty pounds of Hytrel 3078 available from DuPont Engineering Polymers, 713 Chestnut Run Plaza, Wilmington, Delaware, are blended as described above with 30 pounds of an FPO copolymer known as "W209" (available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas) which has been graft polymerized with maleic acid anhydride to contain about 12 % maleic anhydride.

Example 123 - polycycloolefin copolymers

Fifty pounds of "EPO" elastic polyolefin available from Idemitsu Kosan Ltd., Tokyo, Japan, are blended as described above with 30 pounds of an FPO copolymer known as "W209" available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas to produce a polymer blend.

Example 124 - polycycloolefin copolymers

Forty pounds of "Zeonex" multicyclic thermoplastic available from B.F. Goodrich of Akron, Ohio, are blended as described above with 30 pounds of an FPO copolymer known as "W209" available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas to produce a polymer blend.

Example 125 - thermoplastic rubber

Forty pounds of "Vyram 9000" rubber available from Advanced Elastomer Systems are blended as described above with 30 pounds of an FPO copolymer known as "W209" available from Huntsman Polymers Corporation, 2502 South Grandview Avenue, Odessa, Texas to produce a polymer blend suitable for thermoforming.

Consideration must be given to the fact that although the instant invention has been shown and described with respect to certain preferred embodiments it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of the specification. The present invention includes all such equivalent alterations and modifications and is limited only by the scope of the appended claims.

THE CLAIMS

What is claimed is:

1) A polymer blend useful for producing articles of manufacture which comprises:

a) a polyolefin polymer having a heat of fusion between about 0.4 Joules per gram (J/g) to 75 J/g, a polydispersity index of less than about 10, a melt flow rate of between about 0.3 grams per 10 minutes to about 30 grams per 10 minutes at 230 degrees centigrade, and a methyl ethyl ketone soluble fraction content between about 1 and 12 weight percent; and

b) an engineered polymer.

2) The polymer blend of claim 1 wherein said polyolefin is present in an amount between 5% and 95% of the total blend composition.

3) The blend of claim 1 wherein said polyolefin polymer is propylene homopolymer.

4) The blend of claim 1 wherein said polyolefin polymer is a copolymer of propylene with at least one other monomeric raw material having between about 2 and 12 carbon atoms per molecule of monomer.

5) The blend of claim 4 wherein said polyolefin polymer is a copolymer of propylene with at least one other monomeric raw material selected from the group consisting of: ethylene, 1-butene, 1-hexene, or 1-octene.

6) The polymer blend of claim 1 wherein said engineered polymer includes a material selected from the group consisting of: polyolefin homopolymers, polyolefin copolymers, styrene copolymers, styrene homopolymers, natural rubber, isoprene rubber, nitrile rubber, EPDM rubber and EP rubber.

7) The polymer blend of claim 1 wherein said engineered polymer includes a thermoplastic polymer-bearing material selected from the group consisting of: 1) thermoplastic elastomers; 2) thermoplastic polyesters; 3) thermoplastic polyolefins; 4) thermosetting plastics; 5) thermoplastic vulcanizates; 6) cyclic olefin polymers; and 7) graft copolymers of a polyolefin.

8) The polymer blend of claim 7 wherein said graft copolymers include a material produced from graft polymerizing a polyolefin in the presence of at least one monomer selected from the group consisting of: himic anhydride, acrylic acid, methacrylic acid, vinyllic silanes, acrylamide, itaconic acid, fumaric acid or its anhydride, mono or di- alkylated maleates wherein the alkyl group contains between one and four carbon atoms, vinyl amines and amides, and other substituted monomers which contain a vinyl group which is capable of free radical polymerization onto polyolefins.

9) The polymer blend of claim 7 wherein said cyclic olefin polymer comprises a polymer made from a monomeric raw material feed including at least one monomer selected from the group consisting of: dicyclopentadiene, cyclo-octene, tetracyclododecene, and norbornene.

10) The polymer blend of claim 7 wherein said thermoplastic vulcanizate is produced by dynamic vulcanization.

11) The polymer blend of claim 7 wherein said thermoplastic vulcanizate is an elastomeric alloy thermoplastic vulcanizate.

12) The polymer blend of claim 7 wherein said thermoplastic vulcanizate is a melt-processible rubber elastomeric alloy.

13) The polymer blend of claim 7 wherein said engineered polymer is substituted and contains a substituent selected from the group consisting of: halogen, alkyl, phenyl, alkenyl, carboxyl, alkoxy, amino, amido, imino, nitrilo, and styrenyl.

14) The polymer blend of claim 13 wherein said blend has a melt flow rate between about 0.1 grams / 10 minutes and 200 grams per 10 minutes.

15) The polymer blend of claim 14 wherein said Shore (A) hardness of the blend is between about 40 and 200 in the solid state at ambient temperature.

16) The polymer blend of claim 7 said thermoplastic includes at least one substituted or unsubstituted polymeric material selected from the group consisting of: polyacetal, polyacrylates, polycelluloses, polyethers, polyamides, polyolefins, cyclic olefin polymers, polyesters, polyurethanes, polystyrenes, and polycarbonates.

17) The polymer blend of claim 16 wherein said polystyrenes include at least one polymer block selected from the group consisting of: styrene/butadiene, styrene-styrene/isoprene, styrene/ethylene-propylene, and styrene/ethylene-butylene types of polystyrene elastomer block copolymers.

18) The polymer blend of claim 16 wherein said polyesters include at least one polymer selected from the group consisting of: polyether ester block copolymers, thermoplastic polyether ester, copolyether ester, copolyether ester elastomer, block polyether ester, and thermoplastic polyester elastomer.

19) The polymer blend of claim 16 wherein said polyurethanes include at least one thermoplastic polyurethane elastomer.

20) The polymer blend of claim 16 wherein said polyolefin is present in an amount between about 5% and 95 % of the total blend composition on a weight basis.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/21643

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L101/00 C08L23/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 723 546 A (SUSTIC ANDRES) 3 March 1998 see column 3, line 1 - line 56 see column 5, line 49 - line 63 see column 6, line 22 - line 28 see column 6, line 31 - line 40 ---	1-20
X	WO 97 39059 A (WILLEMS EDWIN ; DSM NV (NL); CREVECOEUR GUIDO (NL); SCHEPERS HERMAN) 23 October 1997 see page 3, line 1 - line 26 see page 5, line 34 - page 6, line 4; claims 1,4,5 ---	1-20
A	EP 0 475 306 A (REXENE PROD CO) 18 March 1992 see page 3, line 32 - line 40 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/21643

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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